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DIFFUSION AND STRUCTURAL CHANGES IN MICROCIRCUIT INTERCONNECTIONS

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ABSTRACT

Gold, platinum and gold-on-platinum films, 1000-3000Å thick, were thermally evaporated onto glass microscope slides and given various heat treatments at about 300°C. The room temperature electrical resistivity and spectral reflectivity were observed during the course of the heat treatments. Platinum films show a large decrease in resistivity and a concomitant increase in reflectivity, which are associated with an amorphous to crystalline phase transformation having an activation energy of 10,000 cal/mole for the initial stages. This transformation appears to be oxygen-assisted. Preliminary data indicate a diffusion coefficient for Pt in Au that is near to that of volume diffusion.

I. Introduction

Thin, metallic films are used extensively in integrated circuits for electrodes, for interconnection paths, and for beam leads. In many cases aluminum is successfully used. In other cases, however, aluminum presents difficulties (e.g. electromigration at high current densities), and recourse must be made to multilayers of different metals in order to meet a complex set of requirements. These requirements include the following:

1. good adherence to the substrate (usually SiO_2)
2. high electrical conductivity,
3. high reliability after various processing steps, and
4. compatability with microcircuit manufacturing techniques including photoresist and etching procedures.

Certain multilayer metal systems have been identified as promising candidates to satisfy the above requirements.[1-4] However, multilayer conductors are susceptible to interdiffusion, which may lead to device deterioration and failure. In particular, interdiffusion can result in loss of film adhesion to substrate and in a decreased conductivity; these in turn can result in overheating and eventual circuit failure.

In many thin films, diffusion proceeds much more rapidly than in the corresponding bulk material. This is presumably due to the larger proportion of defects (vacancies, grain boundaries, etc.) in the films. In other cases, diffusion is similar to bulk. Hence, film structure (and film deposition technique) influences the diffusion and ultimately, the device reliability. It is therefore useful to investigate the interdiffusion of thin film metal couples. Rather than employ a "model" or laboratory couple, we have elected to study a practical couple, Au-Pt, because of its present, and potentially large, use in

beam leads and because it appears to meet the requirements listed above. The Au-Pt system also has metallurgical characteristics not possessed by those thin film couples in which diffusion has already been reported in the literature: the Au-Pt phase diagram[5] has a large solid solution miscibility gap and no compounds. With respect to diffusion, one might anticipate the behaviour of such a system at moderate temperatures (200-400°C) to be similar to any two-phase alloy with similar terminal solid solubilities, even though such a two-phase alloy may occur through a eutectic or eutectoid reaction rather than a miscibility gap. However, it is necessary to verify the behaviour of the Au-Pt couple experimentally since many subtle factors interact unpredictably.

The purpose of this program is, therefore, to investigate the interdiffusion of Au-Pt films.

The principal observational parameter is spectral reflectivity. Experimental samples are fabricated by vacuum deposition of a Pt film onto a glass substrate (microscope slide or oxidized silicon wafer) followed by deposition of a Au film.

In our previous work, two unexpected effects prevented clear-cut analysis of the diffusion data. The first effect was a loss of adhesion during the diffusion heat treatment. The second effect was an increase in reflectivity, and in electrical conductivity, of the Pt films in the early stages of the heat treatments; this effect seems to be related to a structural change of the film, and is not related to interdiffusion since it occurs in Pt films alone.

This report summarizes experiments relating to the changes in the Pt films, and to diffusion in Au/Pt film couples.

II. Apparatus

A metallurgical microscope was adapted for the reflectivity measurements. The light source is a one kilowatt tungsten-iodide lamp that illuminates the entrance slit of a monochromator. Either a grating (Bausch and Lomb) or a prism (Perkin-Elmer) monochromator is used. The monochromatic output enters the side-illuminator of the microscope. An objective lens is chosen so that a spot 2 mm. in diameter on the specimen is illuminated. This area is large enough to average out defects such as pinholes, yet small enough to avoid large-scale variations such as film wrinkling. The detector is a silicon solar cell overlapping the eyepiece exit lens and intercepting all the output light. The detector is shielded from ambient and stray light. A 1000 ohm shielded load resistor is placed across the solar cell, and the voltage developed across the resistor is read on a Hewlett-Packard 419A DC Null Voltmeter.

An attempt was made to increase the detector sensitivity by using a phototransistor in place of the silicon solar cell. However, insufficient linearity with light intensity at low values was encountered, and the silicon solar cell was utilized for all measurements.

III. Specimens

The Pt and Au films were deposited on 2.54 cm x 7.62 cm glass microscope slides by successive thermal evaporation in a bell jar at pressures about 2 x 10^{-5} torr. The evaporations were made by electron-beam heating from graphite crucibles during a single pump-down cycle. Substrate temperatures were near 150°C for the first deposit (Pt) and ambient temperature for the second deposit (Au). After the Pt film was deposited, the substrate was cooled by thermal conduction to water-cooled posts over an interval of about ten minutes. Ambient temperatures for the Au were used to minimize diffusion during the specimen preparation.

The microscope-slide substrates were masked during the film depositions (the mask position was changed between Pt and Au films) so as to produce an array of three sets of three rectangles, each rectangle being 2 cm x 0.7 cm and aligned with its long side parallel to the long side of the slide. The outer rectangles of each set of three across the 2.54 cm dimension consisted of Au on Pt couples; the middle rectangle was split into separate Pt and Au monitor specimens, 1 cm x 0.7 cm. Because of the geometry in the bell jar, the film thicknesses differed among the sets. The thicknesses were determined with an interference microscope after evaporating an Al film over part of the specimens.

Normally, a shutter was in place between source and substrate prior to the Pt evaporation. Omission of the shutter has led to erratic behaviour of the resistivity and reflectivity upon subsequent heat treatment.

For certain resistivity measurements, especially for Pt films, specimens were made in a zig-zag pattern and Al contact pads were evaporated over the ends. The pattern is similar to two rectangular"pulse" shapes, 10 mm x 4.5 mm, separated by 4.5mm. The film length is therefore, 62.5 mm, and the film width is 1.5mm. Three such patterns were deposited simultaneously on a 2.54cm x 7.62cm microscope slide.

IV. Resistivity Measurements

The room temperature electrical resistivities of the Au and Pt films have been measured as supplementary data to the optical reflectivity. Resistivities of Au/Pt couples were not taken, since the interpretation of such data is difficult in view of the unknown resistivities of the unknown microstructures existing in the heat treated couples.

Room temperature resistances were initially measured with a four-point probe, usually employed for semiconductors. The probe tips are polished tungsten, and the tip spacing is 0.025 inch. An advantage of this method is that electrical leads, or contact pads, do not have to be attached to the specimen. However, this technique was abandoned because of its destructive nature (holes were scraped in the film) and the need for many measurements over a series of heat treatments. The four-point probe data indicated the following:

1. as-deposited films greater than 1000 Å thick typically have resistivities of 3μΩ-cm for Au and 150μΩ-cm for Pt.
2. Upon heat treatment in air for brief periods (10-30 minutes) at temperatures of 250-400°C, the resistivity of Au films decreased slightly (about 10%) whereas the resistivity of Pt films decreased by a factor of two or more.

More extensive measurements, using the zig-zag film pattern, were made on Pt films ranging from 750 Å to 3400 Å in thickness and with heat treatments up to seven hours at temperatures of 150-325°C. Table I summarizes most of the resistance data taken on these specimens. Figure 1 presents typical resistance-time semi-log plots made from the heat-treatment data. In all cases, there are two distinct regions: an initial rapid decrease in resistance followed by a second, much slower decrease. These regions were approximated by straight line functions, and were characterized by "time constants" τ_1 and τ_2 (first and second regions, respectively) according to the equation $R = R_o e^{-t/\tau}$. In

most cases, only a maximum value for τ_1 could be determined, since (1) the minimum time period for heat treatment was about 10 minutes (due to thermal inertia of the specimens), and (2) the initial reaction is substantially over within 10 minutes (see, for example, specimen 9B in Fig. 1). Figures 2 and 3 are plots of the $\ell n\ \tau_1$, and $\ell n\ \tau_2$, respectively, as functions of 1000/T. Although the points scatter considerably, a least squares treatment of the data was carried out assuming equations of the type $\tau = \tau_o e^{E/RT}$, where E = an activation energy and R = the gas constant. Both τ_1 and τ_2 appear to have nearly the same activation energy, 10,000 and 8,600 cal/g-atom, respectively. However, τ_{01} is 1/4 second whereas τ_{02} is 70 seconds. Attempts to reduce the scatter and separate the data of Figs. 2 and 3 by film thickness and initial resistivity were unsuccessful. More success was achieved by grouping the data in three sets (A, B and C) corresponding to the positions of the specimen on the slide (see Table I). Although film thickness decreases from A to C in all cases, the thickness and resistivity values vary among specimens in each position. Structural differences associated with positions A, B and C seem to be more significant than differences due to thickness or resistivity, perhaps because of our source-substrate geometry. (The evaporated atoms make incident angles of 8°, 22° and 29° with the normal to the substrate at positions A, B and C, respectively.) This may be related to angle effects such as are reported in Ref. 6.

With only a few data points omitted, the slopes of lines drawn through points of corresponding positions appear to agree with the least squares slope in Fig.2. (Data points for specimens 30 and 31, which were differently prepared from the other specimens are not plotted in Figs. 2 and 3.)

Similar groupings of data in Fig. 3 do not all seem to follow the least squares line. B and C specimens tend toward a line giving an activation energy

of about 22,000 cal/g-atom and a value of τ_{02} about 7×10^{-4} second.

Electron microscopy and selected area electron diffraction at 120 kV have shown that the as-deposited films are amorphous. After heat treatments such as above, the films become at least partially crystalline; the diffraction pattern consists of many sharp rings (some are slightly speckled, indicating relatively few crystallites of that orientation), and the image in the electron microscope is about 50% amorphous background and 50% grains of a wide size distribution, with an average size of roughly 20Å.

Rate theory, and nucleation and growth theory are being applied to this data, as has been done for alloy films,[7,8] for Ge[8], Sn[9], and Au[10].

Two further observations make these Pt film, air-annealing, phenomena seem unusual: (1) reflectivity changes (indicative of resistivity changes) are not observed on Pt films with a Au overlay, and (2) annealing the films in vacuum does not produce the marked resistivity changes. It is, therefore, speculated that air, and most probably its oxygen component, plays a major role in the observed rapid structural change at these low temperatures. It should be noted that: PtO dissociates at 550°C and is a violet-black material; some of the Pt films appeared slightly bluish after prolonged heating at high temperatures; PtO_2 melts at 450°C; other oxides are known to be relatively unstable, i.e. Pt_3O_4 and PtO_3. Additional experiments are underway to investigate the role of oxygen.

V. Optical Spectral Reflectance Measurements

Concurrent with the resistance measurements, room temperature reflectance at 6000 Å was measured on the zig-zag Pt films after the various heat treatments. The absolute reflectance at normal incidence was found by reference to an Al film "standard". Typical curves of reflectance (normalized to time zero) versus time at the heat treatment temperature are shown in Figs. 4 and 5. In general, the reflectance changes are similar to the first resistance changes, but do not follow the second resistance changes. Inasmuch as the reflectance depends upon "local" properties, whereas the d.c. resistance depends on both local and long-range properties, one is led to the following model. The initial, rapid, large changes are caused by nucleation of a crystalline phase from an amorphous phase, thus changing the local resistivity of the material and both the resistance and reflectance. The second, more gradual, decrease in resistance corresponds to growth of the crystallites, thereby eliminating some of the remaining amorphous material, and/or eliminating grain boundaries, but leaving the intragrain resistivity unchanged. In this case, the reflectance would be relatively insensitive to the second-stage changes in structure.

The initial rates of change of reflectance (obtained as the slope of the line from the origin to the first measured data point on normalized reflectance versus time plots, such as Figs. 4 and 5) were found for specimens 1, 2, 3, 12, and 16, (A, B and C for each) and are plotted in Fig. 6 as a function of reciprocal absolute temperature of annealing. An activation energy for these changes can be deduced from Fig. 6, and the resulting value of 9600 cal/g-atom is in very good agreement with the value 10,000 cal/g-atom found from resistance time-constants τ_1 (Fig. 2). From this standpoint, one might speculate that scatter in the resistance time-constant data may be caused by discontinuities in the film, which in turn are due to an interplay between the crystallization phenomenon and stress-relief in the film.

As mentioned in the previous section, the large changes in reflectance of Pt films do not occur when the films are overcoated with Au. This effect is readily observed by measuring the reflectance through the glass substrates. Figure 7 is a typical example (specimen 1A).

After some understanding of these changes in the Pt films had been gained, attention was redirected to the interdiffusion in Au/Pt film couples. Toward this end, the spectral reflectance of the Au film on the couples was measured as a function of heat treatment time and temperature and as a function of wavelength. Since each slide was heat treated at a single temperature (for varying times), and since each slide has three specimens of varying thicknesses, a wide range of diffusion conditions was obtained.

Some of the data are presented in Fig. 8. The slides 2 and 3 were heat treated in air at 400°C and 450°C, respectively. Most of the reflectance changes are linear in log time. These have not yet been analyzed. The lowest data points, marked with circled crosses and barred crosses, do not show any trends; these data were from films that had partially lost adherence to the substrate (see section VI, this report). It should be stated that slides 4 and 5, heat treated in air at 400°C and 425°C, respectively, showed only very slight trends toward lower normalized reflectance with increased time, in contrast to slides 2 and 3. This behaviour is not understood as yet.

Figure 9 presents the normalized spectral reflectance versus wavelength of both Au and Pt films, separately and in diffusion couples, before and after a 3.75 hour heat treatment in air at 450°C. These curves are typical of data taken on many other specimens. The significant observations are:

1. Both Au and Pt monitor films change slightly. (Note that the normalization has eliminated the large change in reflectance of the Pt film on heat treatment. This was done so that the wavelength variations of reflectance would be more apparent.)

2. The Pt film of the couple does not change significantly compared to the monitor Pt.

3. The Au film of the couple changes significantly compared to the monitor Au.

The third observation above appears to be related to the interdiffusion process, and is the subject of continuing investigation.

VI. Adhesion

Even at heat treatment temperatures as low as 100°C, we have noted that the Au/Pt couples develop mounds (small spherical protrusions) with corresponding loss of adhesion to the glass substrate. The phenomenon occurs more readily with the thicker films (> 2000Å). It does not occur on either the Au or Pt film monitors (deposited on the substrate simultaneously with the couple). Investigation of this phenomenon has been temporarily set aside in favour of the diffusion studies.

VII. Film Structure

Pt films in the as-deposited and in the heat-treated conditions were examined by transmission electron microscopy and electron diffraction.

An as-deposited film gave a relatively smooth contrast-free image with occasional small bumps up to 60,000X magnification (at 120 kV). The electron diffraction pattern consisted of a few very broad halos, similar to patterns from amorphous materials.

A heat-treated film (5 hours at 250°C, final resistivity 54 μΩ-cm) gave an image at 60,000X consisting of a matrix (or featureless background) and small, uniformly distributed, islands resembling crystallites. The islands occupied about 50% of the area, and had a wide range of sizes averaging about 20Å. The electron diffraction pattern consisted of many well-defined rings that were somewhat speckled, similar to patterns from polycrystalline materials that have an insufficient number of randomly oriented grains to yield smooth rings.

These data further confirm the structural changes of the Pt films.

VIII. Diffusion

Because of scatter in the data, we have not yet been able to extract reliable estimates for diffusion coefficients or activation energies. Specimens on the same slide often do not exhibit regular progressions in reflectances with respect to their thicknesses. In several cases, it appears that the diffusion penetration of Pt into Au tends to be more linear than parabolic, i.e. $x \sim t$ rather than $x \sim t^2$.

From the normalized spectral reflectance (NR) vs wavelength curves, we formed a figure of merit, $NR = (NR)_{0.8\mu} - (NR)_{0.6\mu}$. This figure of merit is useful in characterizing the marked change of the Au-couple curves after certain heat treatments (see Fig.9). Pt appears "white" because its reflectance is relatively uniform across the visible spectrum (0.4 - 0.7 microns). The color of Au is associated with increased absorption (lower reflectance) at the shorter wavelengths. A Au-Pt alloy would then be expected to have a spectral reflectance behaviour between that of Au and Pt (such as exhibited after heat treatment in Fig. 9). No data on spectral reflectance vs composition is available for the Au-Pt system, and so we do not know the composition of the surface alloy corresponding to the observed reflectances after heat treatment. Some idea of this data might be obtained from Reference 11 for the case of Au-Pd, although Au-Pd does not have the solid solution miscibility gap of the Au-Pt system.

For relatively small concentrations, variations in concentration do not have a large effect on the error function, and on the value of the diffusion coefficient, D, as calculated from simple one-dimensional diffusion theory assuming: D is a constant, the surface concentration of diffusing species is held at unity, and the initial concentration is zero in the bulk. Consequently, we have assumed that the first, marked, changes in normalized reflectance might correspond to a surface concentration of 0.10 Pt in

Au. Values of D calculated on this basis are not inconsistent with a mechanism of volume diffusion. Specimen 2B, by happenstance, has curves of normalized reflectance vs wavelength (for numerous times of heat treatment) that appear to depict the diffusion time necessary to just change the "before" to the "after" (as in Fig. 9). From these data for specimen 2B: thickness of Au = 1090Å, time = 19 hours, T = 400°C, one may compute the value 3×10^{-16} $cm^2/$ sec for D. Although this agrees with the value calculated for volume diffusion from the data given in Reference 12, such agreement must be regarded with some scepticism at the moment.

Marked changes in the spectral reflectance vs wavelength of the Pt side of the couples have not been observed. This means either that the value of D is much less for Au in Pt than for Pt in Au, or that the spectral reflectance is relatively insensitive to composition for Au-Pt alloys rich in Pt.

IX. Future Work

Additional experiments will be conducted to determine the role played by O_2 (or N_2) in the structural changes that occur in platinum films upon heat treatment at relatively low temperatures.

Further work will be carried out to determine the diffusion constants and activation energy associated with the interdiffusion between Au and Pt in thin film couples.

If time permits, an investigation will be made concerning the mechanisms involved in the loss of adhesion to the substrate of Au/Pt couples relative to the good adhesion of the separate metal films.

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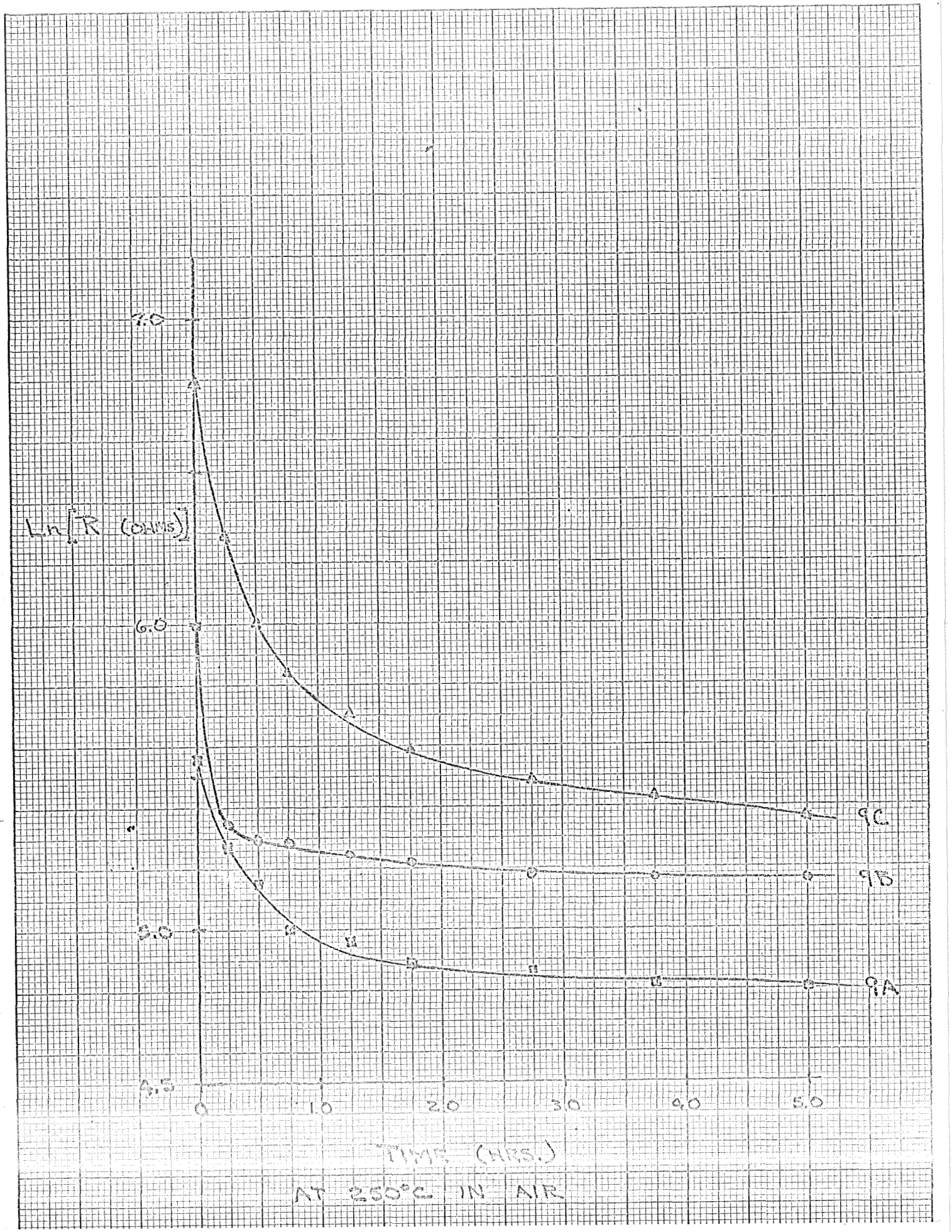
TABLE I

Summary of Resistance Data

Specimen	Thickness (Å)	τ_1 (hrs)	τ_2 (hrs)	T (°C)	ρ_i ($\mu\Omega$-cm)
9 A	1880	0.90	38	250	117
B	1350	0.3	47	250	130
C	1050	0.50	19	250	224
11 A	3330	2.3	40	300	196
B	2800	1.5	25	300	292
C	1020	1.2	27	300	282
12 A	3400	0.24	26	325	107
B	2600	0.24	66	325	134
C	1450	0.16	--	325	174
16 A	1900	0.17	10	275	220
B	1660	0.14	40	275	362
C	750	0.13	53	275	464
27 A	2100	7.4	150	235	138
B	1500	4.3	330	235	220
C	1050	3.1	360	235	460
28 A	3100	5.1	--	265	260
B	1900	2.4	67	265	314
C	1400	1.1	100	265	748
*30 A	2530	0.65	--	250	216
B	2000	0.70	560	250	322
C	1400	0.90	105	250	560
≠31 A	2900	1.9	37	250	248
B	2260	1.4	--	250	396
c	850	1.3	834	250	418

* deposition at 300°C + 20min. at 300°C after deposition (in situ)

≠ deposition at ambient temperatures



10 X 10 TO ½ INCH 46 1470
7½ X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Fig. 1: Room temperature electrical resistance vs annealing time, typical semi-log plots. Pt films, Air annealed at 250°C. Film thicknesses: A) 1880Å, B) 1350Å C) 1050Å.

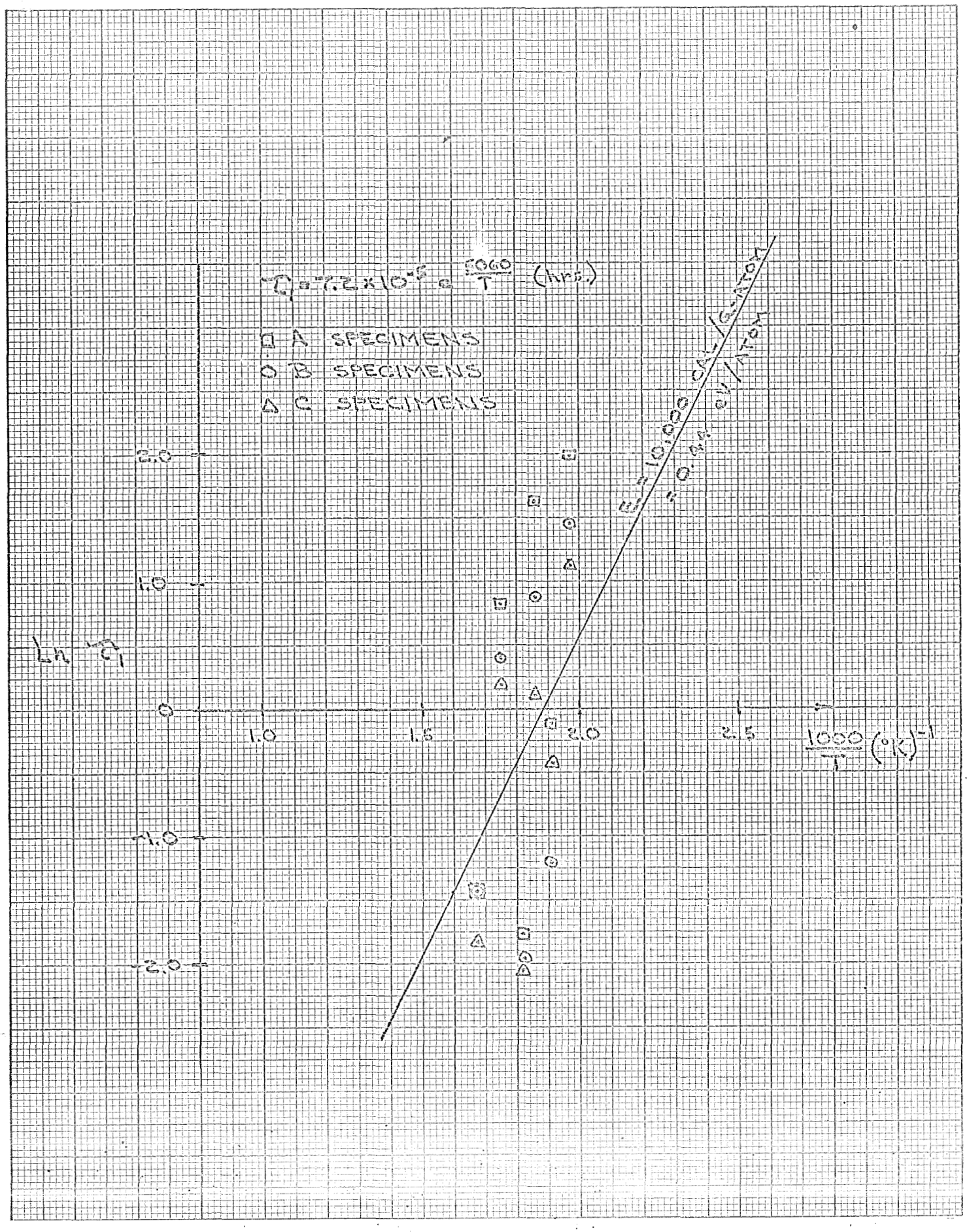


Fig. 2: Time constant of initial decrease of resistance vs reciprocal temperature of air annealing. Pt films.

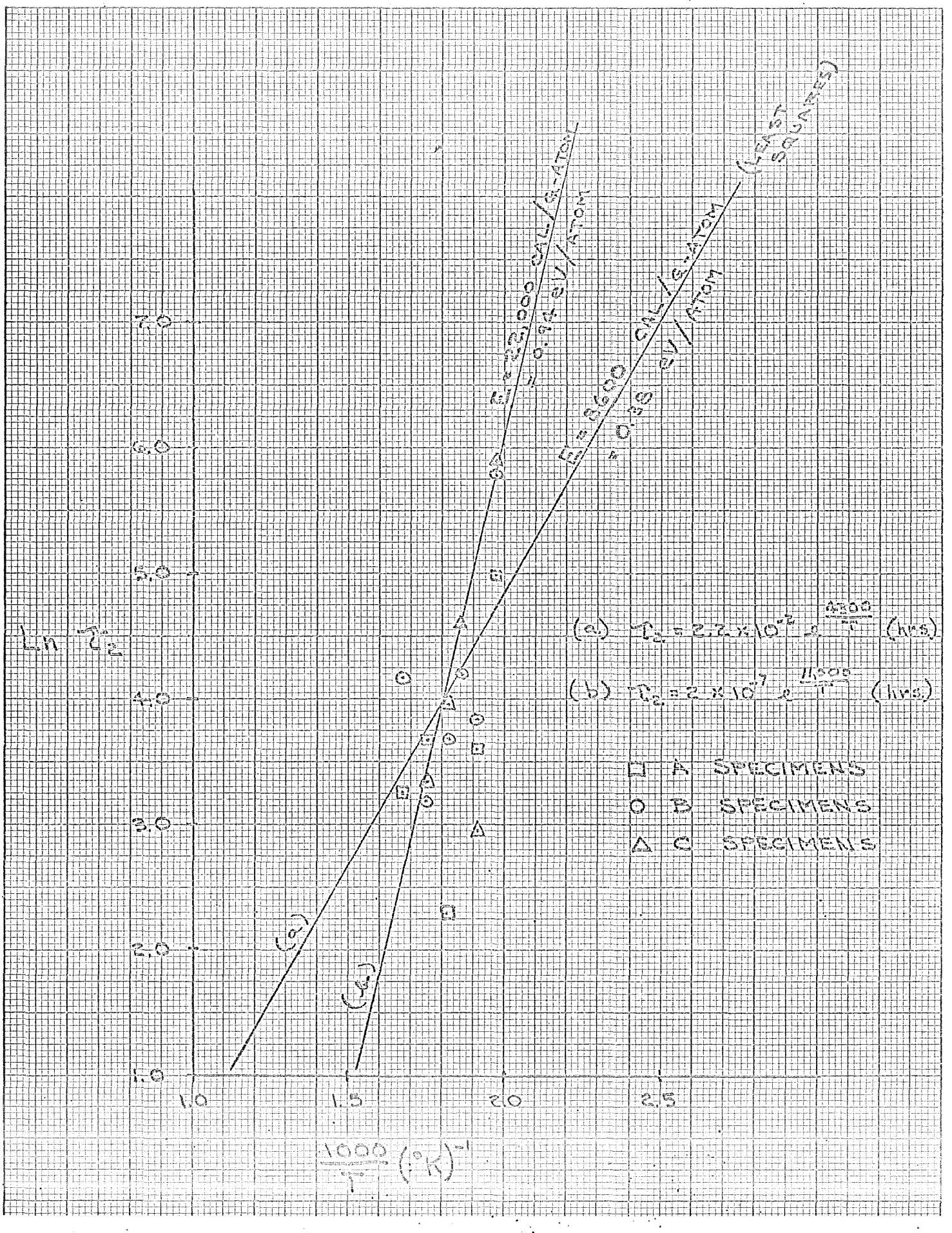


Fig. 3: Time constant of secondary decrease of resistance vs. reciprocal temperature of air annealing. Pt films.

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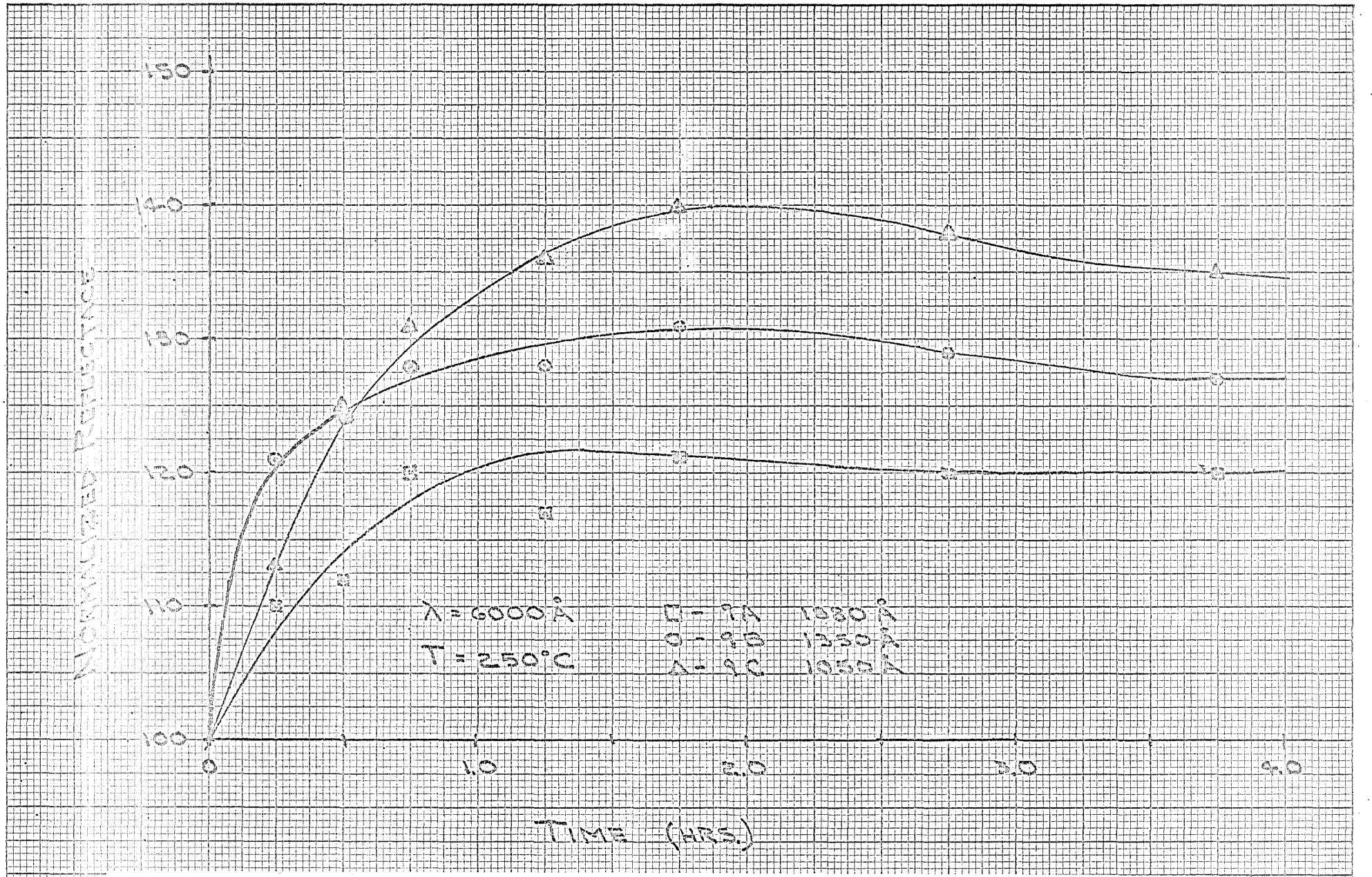

Fig. 4: Normalized reflectance at 6000 Å vs annealing time. Pt films. Air annealed at 250°C.

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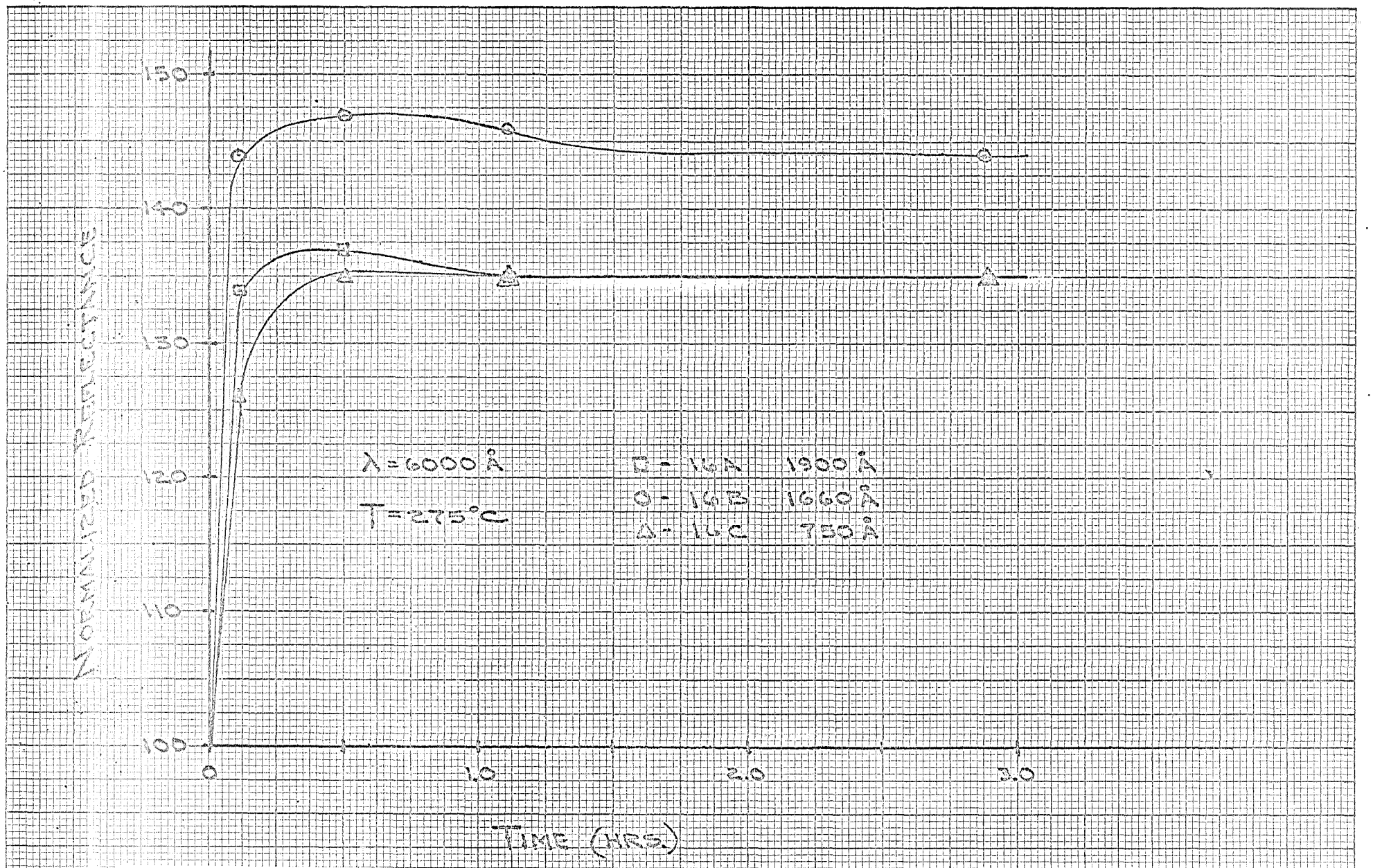

Fig. 5: Normalized reflectance at 6000 Å vs annealing time. Pt films. Air annealed at 275°C.

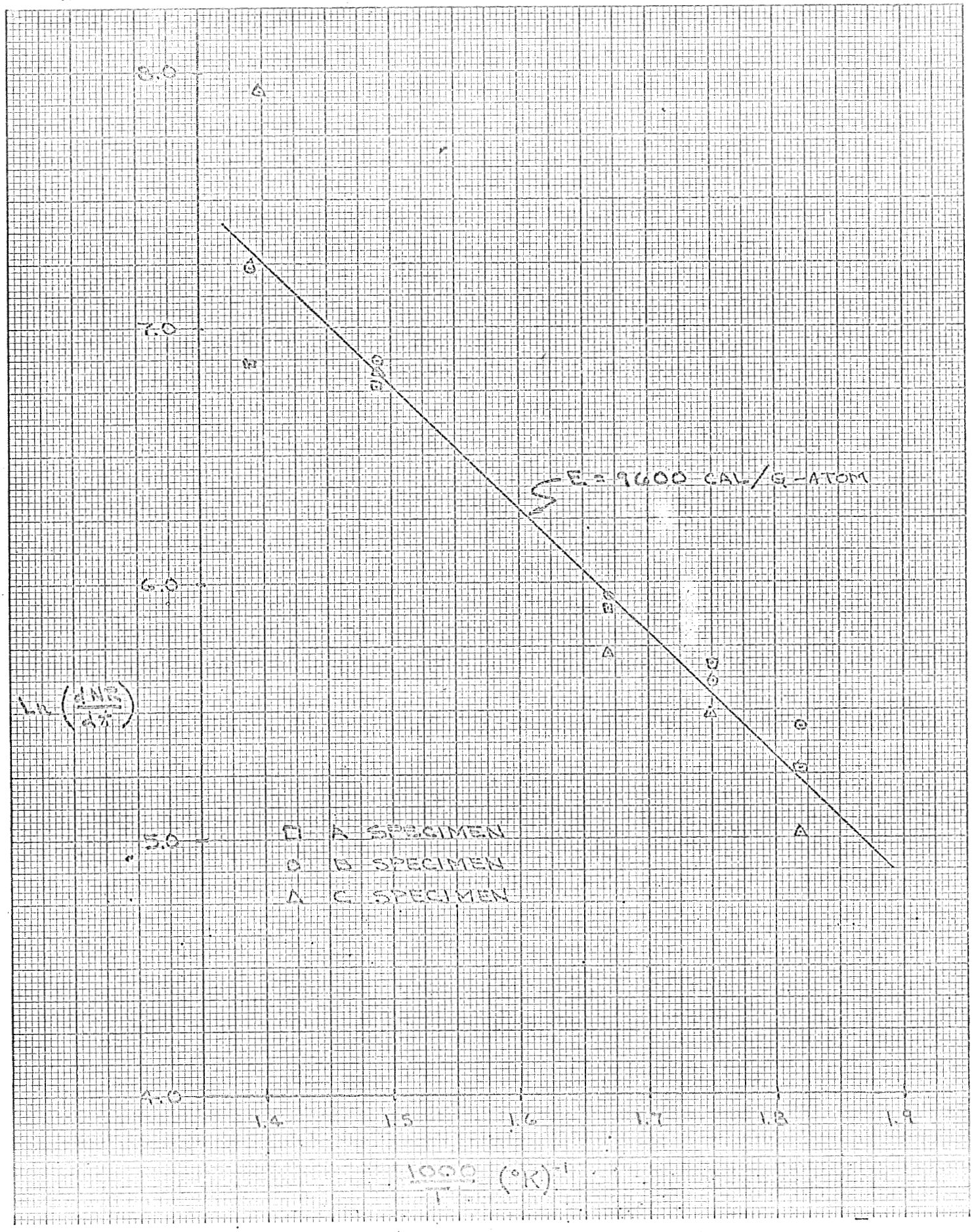

Fig. 6: Initial rate of change of normalized reflectance (at 6000Å) vs reciprocal temperature of air annealing. Pt films.

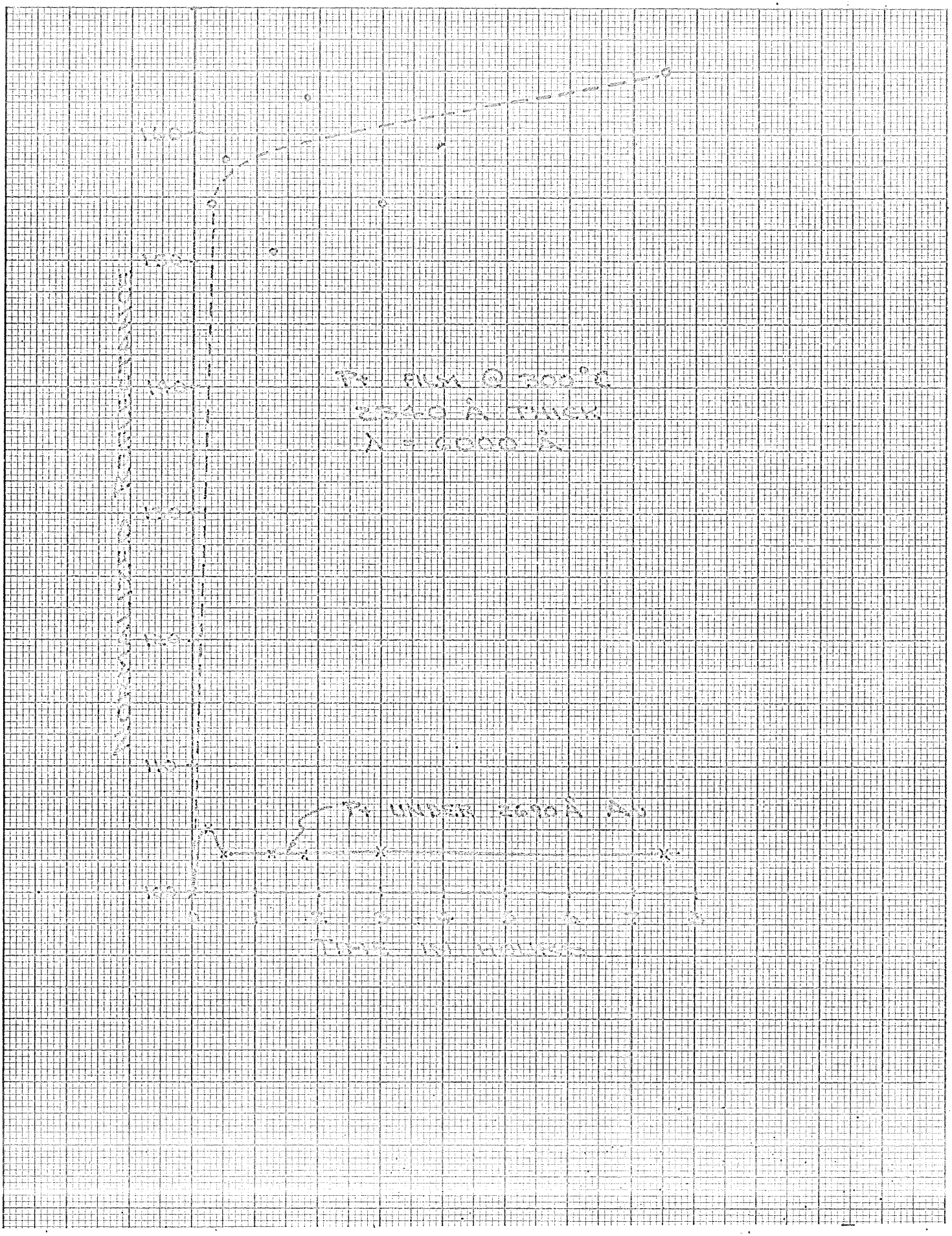

Fig. 7: Normalized reflectance at 6000 Å vs annealing time. Specimen 1A air annealed at 300°C. Data taken through the microscope slide substrate. Pt films.

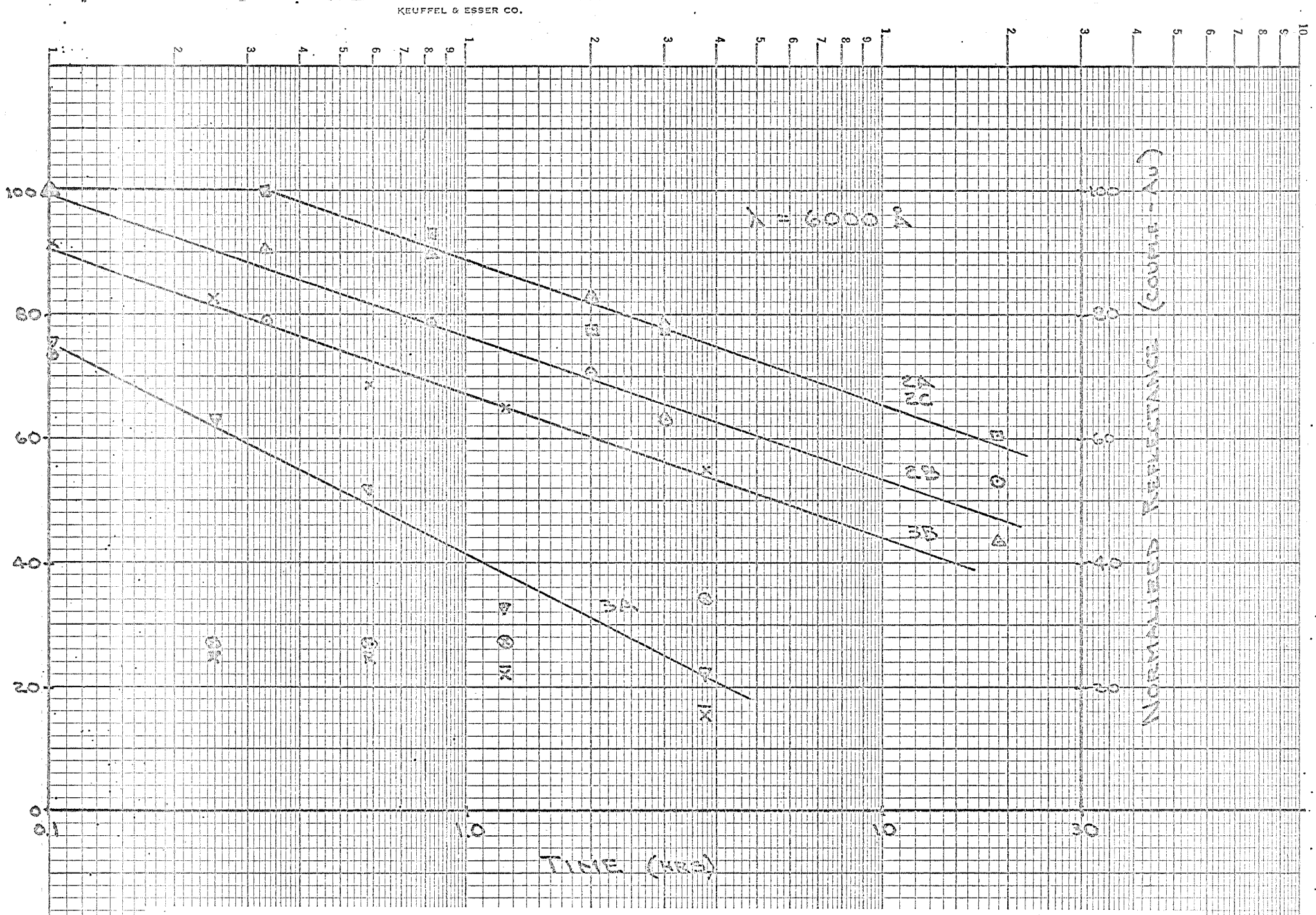

Fig. 8: Normalized reflectance of Au at 6000 Å vs annealing time. Specimen 2 air annealed at 400°C, specimen 3 at 450°C. Au film on Pt film.

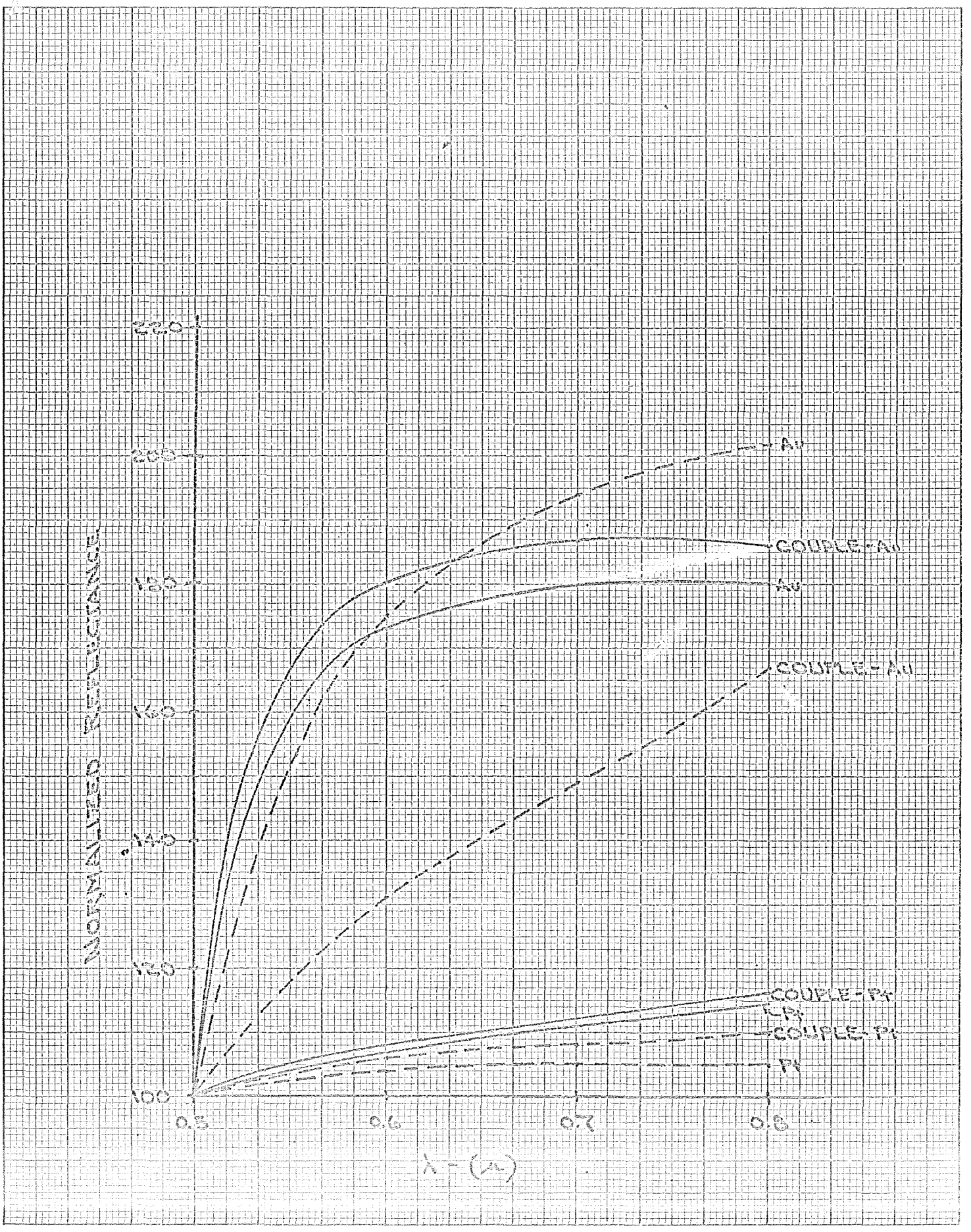

Fig. 9: Normalized reflectance vs wavelength. Au,Pt, and Au-on-Pt films before (solid curves) and after (dashed curves) air annealing for 3.75 hours at 450°C. Specimen 3B.